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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Contributions of natural and anthropogenic sources to ambient ammonia in the Athabasca Oil Sands and north-western Canada" *by* Cynthia Whaley et al.

Cynthia Whaley et al.

cynthia.whaley@canada.ca

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[CW] Thank you for your thorough review of our paper. We have taken into account all of your suggestions, and it has greatly improved the revised manuscript. Please see below for item-by-item responses to each comment (our responses start with "[CW]"). Please also find the revised manuscript attached for reference to the line numbers we mention. We will also be uploading the manuscript with changes tracked.

Reviewer #1's comments:

Citations of non-available papers are given (cited as "this issue" but non available in the

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special issue). This stands for example for description of measurements (Wentworth et al), deposition of N and S (Makar et al), parameterizations (Akingunola et al), fire emissions (Zhang et al.).

[CW] This is one of the difficulties with having a number of linked papers being submitted at the same time. We have modified the text to only refer to the papers which have been submitted at the time these revisions have been carried out. Some of these citations have been submitted to the special issue (e.g., Makar, Zhang), and should appear on ACPD soon. When they are not (e.g., Akingunola, Wentworth), the references were removed.

NH3 concentrations are really low in the region of study and the reader may wonder why this region is worth studying, in the light of what is written in the introduction, (NH3 may be harmful for air, water quality, or ecosystem and human health). A sentence or 2 on the relevancy of studying regions where concentrations remain low for the moment would be useful.

[CW] While the NH3 concentrations are relatively low (0.6 ppbv), the impact on atmospheric chemistry may be large, via the formation of particle ammonium nitrate and ammonium sulphate, and through acidifying emissions. It has been shown that ecosystems in Northern Alberta and Saskatchewan are sensitive to nitrogen deposition, and that dry deposition of NH3 and NO2 dominate the near-source N deposition, while wet deposition of ammonium ions dominate the long-range transport ammonia budget (Makar et al 2017, this ACPD issue). The amount of gaseous ammonia in the atmosphere is thus crucial for accurate estimation of the deposition of nitrogen in the region. It has also been shown the emissions of other pollutants from the AOSR are comparable to that of a city (e.g., Liggio et al, Nature, 534, 91-94, 2016), thus, even where NH3 concentrations are relatively low, it is important to understand if the OS facilities are causing critical levels of NH3, and if not, if any other kinds of sources (e.g., fires, re-emissions) are. This justification has been added to the revised manuscript (lines 63-69).

Some citations are given for satellite measurements of NH3 concentrations at a large scale, but nothing is said about orders of magnitude. Do the model results of this study match with previous satellite measurements? More values of ambient concentrations should be cited.

[CW] The model results of this study match the magnitude of NH3 given by TES in the Shephard et al (2015) paper. The model values in southern part of our domain also match the high end of values reported by NH3 reports (e.g., ref AMoN report for NH3 levels in agricultural and other regions). We have added this additional discussion to the revised manuscript (lines 80-85, 484-486). Clarisse et al (2009) and Van Damme et al (2014) report on IASI NH3 global measurements – however these are total columns, thus harder to compare to the CrIS profiles and surface concentrations in ppbv. Zhu et al (2013) also use TES, but their measurements focus on the U.S., thus would be redundant and less relevant study than the Shephard et al (2015) study mentioned above. Similarly Beer et al (2008) also use TES and focus on the U.S. and China. Low NH3 observations were also shown in the Supplemental Information of Kharol et al (2017, GRL), but these were for Alaska and Yukon, and from the CrIS satellite, so would be redundant to mention.

This is also true for bidirectional exchanges: some papers are cited, but only as a list of papers, and no quantified values are given to be compared with what is found in this study. The papers should be cited with precise examples of measured fluxes is the same area or in regions with the same type of ecosystems.

[CW] Zhu et al (2015) found with GEOS-Chem that the re-emission of NH3 added around 1 ppbv to NH3 concentrations globally in the month of July in North America (but decreased concentrations during the cooler months), and that bidirectional flux did not increase NH4 wet deposition. Wichink Kruit et al (2010) found something more similar to us in their 2007 European study, which was a decrease in NH3 deposition, but an increase in wet NH4 deposition. We have added this information, along with some quantitative comparisons to other sources in the literature (e.g., Kharol et al

(2017); Behera et al (2013), into our discussion in Section 5 (lines 603-607, 631-362, and 644-652).

A meteorological description of the site would be useful all along the study. Indeed, emissions have their impact on NH3 concentrations, but wind speed, humidity, temperature have also a significant impact on exchange fluxes. This part of dynamical interpretation on deposition fluxes is missing.

[CW] The meteorological description and discussion of the region and its impact on bidirectional flux is now added to the revised manuscript, in Sections 2.2 (bidi description), 3.1 (surface site description), Section 5.2 (effect on deposition), and the conclusions.

A discussion about why the addition of bidirectional flux is so important in improving the model is missing in terms of processes. The discussion is only about ppb and %, and not about processes.

[CW] Section 2.2 described the bidirectional flux process, and where the temperature dependency comes in (e.g., equation 3), but a lot of the dynamics/meteorology was hidden in the resistance terms (Ri). We have added additional discussion about how meteorology plays a role to this section (lines 218-230) as well as when discussing deposition in the results section (Section 5.2, lines 639-641). We also added a better explanation of the process at the beginning of Section 2.2, lines 174-179.

2- Does the paper present novel concepts, ideas, tools, or data?: not really, bidirectional exchanges of NH3 is already known to be important, tools and data have already been used in Shepard et al (2015)

[CW] We would argue that our paper presents novel tools (GEM-MACH-Bidi) and data (CrIS observations, and FireWorks emissions): The Shephard et al (2015) study used TES satellite observations and a version of GEM-MACH that did not have bidirectional flux or forest fire emissions. Whereas, in our study, we have used new CrIS satellite

observations and the GEM-MACH-Bidi model, which is a new version of GEM-MACH that has the bidirectional flux scheme (previous GEM-MACH versions had no NH3 re-emission process). GEM-MACH-Bidi is the new tool, which we evaluate with cutting edge NH3 satellite data (from CrIS). We note that ours is the first study to use the CrIS satellite observations of NH3 for model evaluation. Our study is also the first to use the FireWorks forest fire emissions at such high spatial resolution. We have updated the abstract, introduction, and conclusion to emphasize these novel features of our study so that they are clearer for the reader.

11- Is the language fluent and precise? Not always

[CW] The language was made more precise in the revised manuscript, where the reviewer mentioned problems in the detailed comments.

13- Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? Yes, mentioned in specific comments. 14- Are the number and quality of references appropriate? Not always

[CW] When specific comments were made relating to these issues, they were addressed in the responses below.

Specific comments Line 42: As you write that NH3 is a contaminant, precise in what order of concentration it has negative effects.

[CW] While NH3 is poisonous if inhaled in great quantities, these are much greater than found in the atmosphere. For example, there is an Alberta Ambient Air Quality Objective for NH3, which is 2000 ppbv 1-hour average; the basis for this is odour http://aep.alberta.ca/air/legislation/ambient-air-quality-objectives/documents/AAQO-Summary-Jun29-2017.pdf , but this is not relevant to the outdoor atmospheric conditions we are talking about in our study. The reason NH3 was listed as a Criteria Air Contaminant is because of its secondary effects as a PM precursor (Environment Canada, 2001), as discussed in this paragraph of the origi-

nal manuscript. Therefore, one cannot say what ambient concentration of NH3 would cause negative health effects because it is complicated by the atmospheric conditions (meteorological and concentrations of other chemical species) for PM formation. Thus, there is no federal Canadian Ambient Air Quality Standard for NH3, however, there is for PM2.5 (in Canada, the PM2.5 guideline is 28 ug/m3, 24 hour average). Another negative affect of NH3 is its contribution to nitrogen deposition (discussed in the Makar et al companion paper) – wet ammonium ion deposition dominates N deposition in the regions hundreds of km downwind from the anthropogenic sources, for example. The amount of nitrogen deposition which may cause an exceedance of critical loads is highly dependent on the local ecosystem characteristics, and varies by over 3 orders of magnitude in the region examined here. Thus, no particular NH3 concentration can be cited to cause an exceedance in critical loads.

Precise somewhere in your introduction that despite negative effects of high concentrations, low concentration regions are also worth studying.

[CW] It is still important to study this region because the modelled background NH3 must be correct in order to understand the relative impacts of the oil sands operations, and because even a small amount may cause a critical load exceedance for deposition to sensitive terrestrial and wetland ecosystems. This explanation was added to the introduction, lines 63-69.

Line 44: Modeling provides: : :: this could be true if inventories are correct and with fine resolution, which is hardly feasible in most models. Remove this first part of the sentence.

[CW] Done.

Line 55: reformulate your sentence because reading “the AOSR is a large source of air” is a bit weird.

[CW] Done.

Line 58: why are NH3 concentrations so low, despite local pollution?

[CW] The anthropogenic emissions of the AOSR take place in a relatively small region compared to all of "northern Alberta and Saskatchewan", which is where we've said that NH3 concentrations are low. We were basically saying that the area surrounding the AOSR has very few sources of NH3, and as a result, background concentrations of NH3 in that area are low (b/c of little population and lack of agriculture, compared to the southern part of the province. The low background concentration puts into context the $\sim$0.5 ppbv model bias that existed before the addition of the missing sources. We've reformulated those sentences in the revised manuscript (lines 63-65) to better get that point across.

Line 61: give mean concentrations of cited agricultural areas.

[CW] In our reformulation, this reference is removed.

Line 66: give values of the fraction of deposited NH3 compared to NO2 and HNO3.

[CW] Since our references were based on atmospheric concentrations rather than deposition measurements, we have revised the wording here, and given ratios of NH3 to other N gases in the air. See lines 72-76 in the revised manuscript.

Line 114: precise what species are used from the inventories.

[CW] List of 25 species was added to the manuscript (lines 128-131).

Line 121: A word about the importance of carefully design stack parameters would be useful to understand why this part is so important for your study.

[CW] On line 128 of the original manuscript we mentioned that ill-designed stack parameters resulted in "erroneous short term plume events", causing "NH3 levels up to 2 orders of magnitude higher than ground observations", which should be explanation enough for the importance of stack parameters. However, we have added a note in the revised manuscript (line 148) that this stack is in the AOSR, thus it is important to get

right for our study.

Line 167: give reference values of realistic NH3 concentrations consistent with findings from the literature, and explain why you use low end values.

[CW] We referenced annual AMoN values for “realistic NH3 concentrations” (line 209). The explanation of why the low end values were chosen was already given – to get realistic NH3 concentrations compared to observations.

Line 191: what do you mean by “major point emissions?”

[CW] An explanation of area and major point emissions has been added to the Emissions Section (Sec 2.1), lines 137-140.

Line 220: what is ECCC?

[CW] Acronym is now defined upon first use.

Line 259: you mention +/- 15% of uncertainty for measurements, with a mean measured value of 0.63 ppb (line 59). The model/measurements bias is 0.3-0.85 for bidi, what is the real impact on modeled concentration? What is the range of possible concentration? Is the measured concentration included in this range?

[CW] For the AMS-13 model evaluation (a single site heavily influenced by local anthropogenic sources), a 15% error on the measured 0.63 ppbv average is only 0.0945 ppbv, giving the range of 0.536 ppbv to 0.725 ppbv for the average measured concentrations there. The median model bias of the base case is -0.35 ppbv, meaning that the model reports only 0.28 ppbv NH3 in that area – well below the bottom of the measurement range. The bidi model had a +0.3ppbv bias, meaning that the model reports 0.96 ppbv in that area, which is well above the range in the measurement average. Taking the standard deviation of the model biases at that specific location into account, and they all overlap with the measurements (e.g., the vertical range in the whiskers in Figure 5). However, we see in Figure 6, that the real improvements come in the form of better correlation and slopes with the bidi and fire+bidi models. We have not added

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any new text, as the existing text covers all of this.

Line 299: Figure 3 should not be placed here. It is only used later in the text, and should be included before figure 9. Furthermore, if placed here, it is not understandable why these three dates are chosen (not explained in the caption).

[CW] We have removed the reference to Figure 3 early on, and moved the figure to the appropriate place in the results/discussion.

Line 324: You mention fig 5 and then you talk about fig 4. Place fig 5 after fig 4 and give a description on interpretation of it.

[CW] That sentence about Fig 5 is removed, and figure 5 discussion is now appropriately placed.

Line 326: what are the background times?

[CW] Changed to "when NH3 concentrations are relatively low (< 0.5 ppbv in the base model)".

In figure 4, NH3 is in ppb, but NH4+, NO3- and SO42- are not in ppb. Please correct the caption

[CW] Done.

Line 335: what is the increase of concentration with the influence of a local plume? 0.5 ppb seems to be very very low, and more included in the measurement noise than in a local pollution signal.

[CW] The 0.5 ppbv reference is in regard to the base model (line 334 of original manuscript) – not in the measurements. The base model has very very low background concentrations (which we are correcting in this work), thus any time the base model goes above 0.5 ppbv, we can assume a nearby source, such as a plume. Note that even the measurements did not exceed 3 ppbv, and had a mean of 0.6 ppbv during this time period. Thus 0.5 ppbv is not low in relation to that. Discussion of these

concentrations can be found in lines 387-392 of the revised manuscript.

Line 337: 0.08 ppb is less than the 15% measurement uncertainty. Is it really significant?

[CW] No, you are correct, it isn't. Therefore, we have removed the discussion about removing the plume influence to see "better" results, since they are not significantly better.

Line 339: R=0.1 and 0.4. Are these coefficients significant? Could you give a significance (p-value) of your correlation calculation everywhere it is necessary?

[CW] We have done a paired t-test on the AMS13 surface NH3 data, and found that none of the three model simulations can be considered statistically indistinguishable from the measurements at the hourly time scale ($t>1$, $p<0.05$), although the weekly-averaged bidi simulation comes close, with $t=1.9$, $p=0.15$ (for model to be considered the same as the measurements, t should be <1, and p should be >0.05). These statistics are now included in Table 2 and discussed in the revised manuscript. Since the AMS13 results are just for a single gridpoint at the surface (where local variability due to point sources makes getting a good match closer to sources difficult), we have also added statistics for the aircraft and satellite results as well. The satellite results cover a much larger domain (all of Alberta and Saskatchewan, and throughout the troposphere). For the particulate species, none of the correlations are significant either. Most air quality models do not model PM species well, and this is an area of on-going study.

Line 340: Fig 6a: what is the unit of NH3 concentration?

[CW] Fig 6a has units of ppbv in the axis labels, and the slope of the model/measurement line is unitless. Nothing changed.

Line 368: SO42- is influenced by anthropogenic emissions, why not by fire emissions?

[CW] Added "and fire emissions" here.

Line 375: Why did you choose this precise flight? By the way, it would be useful to give some average values of meteorological conditions when describing the area of study (mean temperature, humidity, rainfall, wind speed, etc: : : all parameters that have a possible influence on NH3 concentration)

[CW] This flight was chosen as an example because this flight sampled mainly background NH3 concentrations (rather than facility plumes), and it is the modelled background NH3 that this study aims to improve (lines 448-450 in revised manuscript). Meteorological conditions for the AOSR were added to Section 3.1, lines 317-329.

Line 376: can you explain why fire+bidi does not improve the results compared to bidi?

[CW] In Figure 7c and d, there is very little difference in concentrations because the flight did not pass through a fire plume. We have added this explanation to the revised manuscript (lines 456-457).

Line 404: Figure 3 is used in this paragraph. It should appear in the text at this time, and not before.

[CW] Done: Fig. 3 of the original manuscript, is now Fig. 8 in the revised manuscript.

Line 430: specify at the lowest level.

[CW] Done.

Line 446: remove “that” before the fire+bidi model

[CW] Done.

Line 451: You suppose that the conversion of NH3 to NH4+ is underestimated: did you have a look at the NH4+ pool in that case?

[CW] Unfortunately, there were no NH4+ measurements in that region to compare to.

Line 453 to 459: this explanation is very confused. Please rephrase.

[CW] It has been rephrased and put into point form, making clear which part of the

discussion is for which explanation (a, b, c) of the bias (lines 549-569).

Line 507: this sentence is not useful. Obviously if bidirectional parameterization is used it will balance deposition with emission and not increase deposition fluxes.

[CW] We agree with the reviewer that using a bidirectional scheme can only decrease net deposition for NH3 compared to a traditional unidirectional deposition scheme if all the other model components/parameters remain the same, e.g., the Zhang et al. (2010) bidirectional scheme versus the unidirectional scheme of Zhang et al. (2003), because the former was built on the later. However, the original unidirectional scheme used in our model was not exactly the same as in Zhang et al. (2003), but a hybrid of Wesely (1989) (for stomatal uptake) and Zhang et al. (2003) (for non-stomatal uptake). Thus, we cannot completely exclude the possibility that the new bidirectional scheme might produce higher deposition under certain circumstances without a model validation.

Line 517 and elsewhere: the unit for the flux is not appropriate. Please homogenize throughout the paragraph and use preferably ngN.m-2.s-1.

[CW] Units of moles/m2/day are now consistently used throughout.

Lines 584 and 587 use another unit which is not a flux unit. In this paragraph needs bibliography values need to be included for equivalent ecosystem or region.

[CW] Do you mean lines 582-583, which talked about % contributions to atmospheric concentrations? No numerical values were written on lines 584 and 587. However, we had included references to reported deposition and discussed them in Section 5.2, lines 524-531 of the original manuscript, using appropriate units. The revised manuscript has flux in moles/m2/day throughout.

Figure 12 and 13 are redundant.

[CW] Figure 12-14 were removed, and replaced with a new Figure 12 that is the total NHx deposition.

Figure 13 is not necessary in my opinion.

[CW] Figure 12-14 were removed, and replaced with a new Figure 12 that is the total NHx deposition.

Line 539: again this sentence is not useful. Obviously wet deposition is only deposition. Again flux units are not correct and should be homogenized.

[CW] Any mention of ïĄ■moles/m2 should have been moles/m2/day. This was corrected in the revised manuscript. Also, most of the discussion is now about total NHx deposition, rather than of wet and dry deposition discussed separately.

Line 550: how do wet deposition fluxes compare with literature?

[CW] It has been difficult to find relevant wet deposition fluxes in the literature, as many of those studies report on ammonium concentrations in rainwater without giving the precipitation flux. Or they report on locations that are not appropriate to compare to Alberta/Saskatchewan (e..g, Murano et al, 1998 found average values of 1E-4 moles/m2/day in Japan). We have however, added a couple of references, including a technical report in the United States, which reported about 2E-5 moles/m2/day average in the U.S. (lines 668-671). Our results are in between the values reported in those two studies.

Line 570-571: this sentence has already been written above. The conclusion should mention the possible influence of meteorological conditions on NH3 concentration, as well as in the text.

[CW] The fact that the NH3 emission factors need to be revisited for further model improvements is an important conclusion of our study, and that is why we have highlighted it again in our conclusion. The meteorological discussion of the region and its impact on bidirectional flux is now added to the revised manuscript, in Sections 2.2 (bidi description), 3.1 (surface site description), Section 5.2 (effect on deposition), and the conclusions.

Line 574: “miniscule”: please quantify.

[CW] 0.02 ug/m3 for each. This was added to the sentence (lines 698-696).

Technical comments Line 16: remove , aftertime period.

[CW] Done.

Line 108: write covers instead of covering, twice in the line.

[CW] Done.

Line 109: remove “And” at the end of the line.

[CW] Done.

Line 117: remove (before Zhang and put (before 2017.

[CW] Done.

Line 163: replace “in” by “from” before Wen et al.

[CW] Done.

Line 228: Time period “from”

[CW] Done.

Line 296: a verb is missing in the sentence.

[CW] The verb was “compute”, but it should have been part of the list. We have fixed the sentence.

Line 321: include “to” after compared.

[CW] Done.

Line 352: remove italics for “should”, same line 488 for “total” and line 507 for “more”

[CW] Done.

Line 454: a) is missing after 10c

[CW] Done.

Line 493: problem with the sentence, please rephrase

[CW] Done.

Line 507 and 509: remove , after 11.

[CW] Done.

Line 526: replace x by times

[CW] Done.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-627/acp-2017-627-AC2-supplement.pdf

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